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RESEARCH GRANT NGR 47-002-041

Final Report

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
NON-METALLIC MATERIALS BRANCH, MATERIALS DIVISION

Langley Research Center
Hampton, Virginia



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TITLE OF RESEARCH: "ISOMER EFFECTS ON POLYIMIDE PROPERTIES"

PERIOD COVERED: September 15, 1972 - March 31, 1978

ABSTRACT: The goal of this investigation has been the preparation of polyimide polymers which are thermally stable and at the same time processable. Asymmetry of substitution, addition of alkyl substituents to an aromatic ring, and an increase in the number of aromatic rings present in the diamine monomer are all parameters which have been explored. It has been shown that the use of an asymmetrical diamine in the preparation of a polyimide produces a polymer with a markedly lowered glass-transition temperature. This is achieved with little or no sacrifice of thermal stability. An alternate approach taken has been to prepare imide monomers which are capable of addition-type polymerization. The complete characterization of these systems has not been completed.

B. L. Stump
B. L. Stump, Principal Investigator

September 15, 1978

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I. Introduction

Heteroaromatic polymers have proven to be among the best organic materials available which possess unusually high thermal stability. These polymers contain hexagonal aromatic rings in the backbone of the chain, and the polymers are formed from starting materials or monomers in which the functional groups are symmetrically substituted on the aromatic ring. A major difficulty with these materials, however, is their lack of solubility and, hence, their limited processability.

This investigation was undertaken initially to explore the effect of a variation in structure on the solubility and glass-transition temperature of polyimide polymers. Either a lowering of the glass-transition temperature or an increase in the solubility of the polymer should lead to improved processability. The results of this investigation, together with those of Dr. Vernon L. Bell of NASA's Langley Research Center, have been summarized in an extensive paper published in 1976 (1). A lowering of the glass-transition temperature was shown to be achievable by making the polymer molecule less symmetrical.

The studies were extended to incorporate not only additional asymmetry but also larger molecular weight in the monomers. Potentially, these monomers should afford high molecular weight macromolecules with fewer imide rings in the polymer backbone, and a further lowering of the glass-transition temperature or an enhancement of the polymer solubility might result.

Finally, an alternate route to thermally-stable polymers through imide monomers that would polymerize or cross-link when heated has been explored. This type of polyimide is called an "addition" polyimide.

II. Discussion

A. Asymmetrical Diamines

This project began as a study of the possible existence of an *ortho* effect. It was felt that compounds like diphenylmethane and benzophenone could be converted to diamines in which the amine groups would be substituted *ortho* to the methylene or carbonyl bridge between the two rings. Such asymmetrical monomers could produce polyamides and polyimides with irregularity in the polymer chain such as to lower markedly the glass-transition temperature of the polymer and perhaps make the polymer soluble.

The investigation called for the synthesis of four diamine monomers: 2,4'-methylenedianiline; 2,4'-diaminobenzophenone; 2,3'-methylenedianiline; and 2,3'-diaminobenzophenone. A study of the polymerizability of these monomers with both pyromellitic dianhydride (PMDA) and with benzophenone tetracarboxylic acid dianhydride (BTDA) to form polyimide products, together with an evaluation of the product polymers, completed the objectives proposed.

The first two monomers, the 2,4'-isomers, were synthesized during the summer of 1972, while the Principal Investigator was a NASA-ASEE Summer Faculty Research Fellow at Langley Research Center. Scouting experiments carried out at that time indicated that 2,4'-methylenedianiline reacted with BTDA to form high molecular weight

polyimide. To this point, there had been some question as to whether an amino group in the *ortho* position in a monomer like 2,4'-methylenedianiline could participate in a polymerization reaction. Eventually, all possible methylenedianilines and diaminobenzophenones with amine groups in an *ortho* position were synthesized and polymerized to polyimides. These syntheses have been described in earlier reports (2,3).

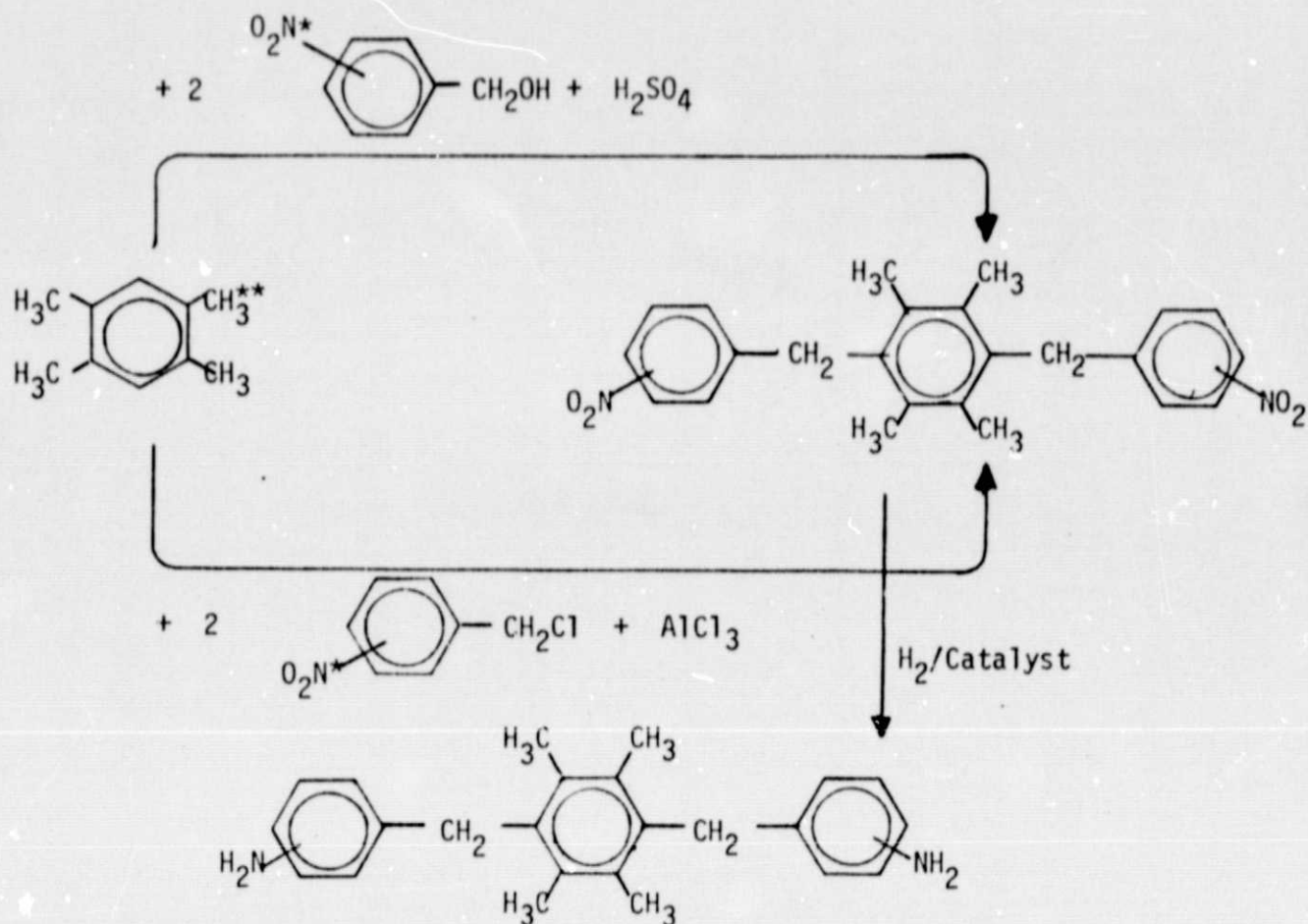
These studies were conducted in cooperation with Dr. Vernon L. Bell at NASA-LaRC and a joint publication summarizing the studies appeared in 1976 (1). It was learned that diamine monomers with the amine groups in the *meta* position on the two aromatic rings lead to polyimides with the lowest glass-transition temperatures. This result was somewhat surprising, since it had been anticipated that a less-symmetrical polymer would result from a monomer with an amine group in the *ortho* position.

While solubility studies were not pursued as a part of this project, an investigation by St. Clair, St. Clair, and Smith (4) has substantiated the existence of an *ortho* effect. They prepared polyimides from the methylenedianilines, as well as from the diaminobenzophenones, the oxydianilines, and the phenylene diamines. The dianhydride monomers used included PMDA and BTDA, together with 4,4'-oxydiphthalic anhydride (ODPA), 2,2-*bis*(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F), 2,2-*bis*[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane dianhydride (BFDA), and 4,4'-*bis*(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (BDSDA). They found that both modification of bridging groups in the dianhydride structures and variation of the amine positions in the diamine isomers affected polyimide solubility. Having an *ortho*-substituted amine group in the diamine monomer even produced soluble or sparingly

soluble polyimide films of BTDA and PMDA. The solvents they used in their studies included N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), N-methylpyrrolidone (NMP), and *m*-cresol.

The search for novel diamines was continued, and the synthesis of a series of aminobenzyl-substituted alkylbenzenes containing three aromatic rings was undertaken. It was thought that these diamine monomers could enhance the properties of product polyimides in several ways. The much larger molecular weight monomer would make possible the synthesis of a high molecular weight macromolecule with fewer imide groups in the polymer backbone. Enhanced solubility and/or a lower glass-transition temperature might result. The alkyl substituents on the central aromatic ring make possible the incorporation of additional asymmetry in the polymer backbone, depending upon their points of attachment on the ring. Finally, the alkyl groups could have a solubilizing effect.

The general synthetic scheme followed in the preparation of these compounds is shown as Figure 1. The benzyl alcohol or benzyl chloride used could be either *ortho*, *meta*, or *para*, and the tetramethyl benzene could be either the 1,2,4,5- (durene), the 1,2,3,5- (*isodurene*), or the 1,2,3,4- isomer. The synthesis of several of these monomers has been described in previous reports (5,6) and the results for these monomers are summarized here in Table I. Little effort has been given to synthesizing the *ortho* compounds, since our earlier studies had shown (1) little promise of an *ortho* effect on the glass-transition temperature of product polyimides. Neither has an attempt been made to mix the points of attachment of the amine groups on the two benzyl rings, *i.e.* *o,m'* or *m,p'*, as was done in the earlier work (1).



*The nitro group in the benzyl alcohol or the benzyl chloride may be either in the *ortho*, *meta*, or *para* position.

**The tetramethyl benzene can be either the 1,2,4,5-, the 1,2,3,5- or the 1,2,3,4-isomer.

Figure 1. Aromatic diamines containing three Benzene Rings.

TABLE I

THE MELTING POINTS OF NITROBENZYL- AND AMINOBENZYL BENZENES
AND THE GLASS-TRANSITION TEMPERATURES FOR PRODUCT POLYIMIDES

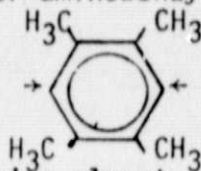
Compound ¹	Nitro Analog T, °C	$\Delta T_p^2 - m$ °C	Amino Analog T, °C	$\Delta T_p^2 - m$ °C	Copolymer ³ with BTDA T _g , °C
1,2-Bis(m-amino- benzyl)-3,4,5,6- tetramethylbenzene	192	$\approx - 20$	125-128	$\approx + 135$	249 (261)
1,2-Bis(p-amino- benzyl)-3,4,5,6- tetramethylbenzene	169-172		260		287 (303)
1,3-Bis(m-amino- benzyl)-2,4,5,6- tetramethylbenzene	152-157	$\approx - 5$	151-153	$\approx + 10$	248 (261)
1,3-Bis(p-amino- benzyl)-2,4,5,6- tetramethylbenzene	147-149		160-162		250 (256)
1,4-Bis(m-amino- benzyl)-2,3,5,6- tetramethylbenzene	227-228	$\approx - 12$	222-223	$\approx + 5$	249 (262)
1,4-Bis(p-amino- benzyl)-2,3,5,6- tetramethylbenzene	214-216		228		291 (342)

¹The diamine monomer is the compound named. The melting points for these compounds are shown in the column labeled "amino analog". The parent nitro compound's melting point is given in the column labeled "nitro analog." These diamines were polymerized in dimethylacetamide solvent with the co-monomer BTDA.

²The $\Delta T_p - m$ refers to the difference in melting points for the *para* and *meta* isomers for each of the compounds shown.

³The T_g values shown in the parenthesis are values obtained by TBA.

The effect of symmetry as to the point of attachment on the aromatic rings in the monomers provides some interesting results. Having the nitrobenzyl- or aminobenzyl- groups symmetrically attached



to the central aromatic ring almost completely off-sets the effect of the point of attachment of the nitro or amino group on the benzyl ring. In fact, in the nitro series the *meta*-substituted nitro groups produce higher melting compounds than do the *para*-substituted groups. The symmetry about the central ring appears to be very important, with 1,3- substitution (*meta*-type) producing the most dramatic effect on the melting point of the nitro compound. In fact, the nitro groups in the *para*-positions on the two benzyl rings produce lower melting compounds than do the nitro groups in the *meta*-positions. The temperature difference is most striking when the benzyl groups are substituted 1,2- on the central ring, i.e. $\Delta t_p - m \approx - 20^\circ \text{C}$.

In the amine series, the effect of symmetry is much more pronounced. The *meta*- rather than the *para*- attachment of the amino functional groups leads to the lower melting compound in each case. However, the point of attachment on the central aromatic ring is again the more important symmetry factor, for the melting point difference between the *meta*- and the *para*- substituted diamines is small. The exception is the melting point difference when the point of attachment on the central ring is 1,2-. The 1,2-*bis*(*m*-aminobenzyl)-3,4,5,6-tetramethyl benzene has an unusually low melting point.

When the diamines were polymerized with BTDA to form polyimides, the effect of the point of attachment on the central aromatic ring is obviously important, for the polymer formed from 1,3-*bis*(*p*-diamino-

benzyl)-2,4,5,6-tetramethyl benzene has about the same t_g , 250 °C, as do polymers formed from the *meta*-diamines, all of which have t_g values of 248 - 249 °C. It was disappointing to find that no additive effect resulted from having 1,3- or *meta*-type substitution on the central ring as well as *meta*-substitution of the amine groups.

The chemical analyses for these compounds are given in Table II.

B. Diamine Monomers with Cross-Linking Potential

The preparation of a polyimide monomer like *m,m'*-diaminobenzophenone, but containing a third amino group in the position *ortho* to the carbonyl group connecting the two aromatic rings, is desirable. This third amino group would be available for post-cure cross-linking to elevate the glass-transition temperature of the processed polyimide product. The reaction scheme followed in preparing this monomer is outlined in Figure 2. The synthesis and characterization of 2-acetamidobenzophenone, 2-acetamido-5,3'-dinitrobenzophenone, and 2-acetamido-5,3'-diaminobenzophenone was accomplished and has been described in an earlier report (7). Conversion of the 2-acetamido-5,3'-diaminobenzophenone to 2,5,3'-triaminobenzophenone presented some difficulty, and it was clear that the triamine was very sensitive to oxygen and had to be handled in an inert atmosphere. For these reasons, it was decided that the *ortho*-amino group would be left in its acetylated state.

A polymer of 2-acetamido-5,3'-diaminobenzophenone with BTDA was prepared by Dr. Bell at NASA-LaRC and evaluated via torsional braid analysis (TBA). The incorporation of the acetamido group in the *ortho* position of the diamine had increased somewhat the t_g of the product

TABLE II

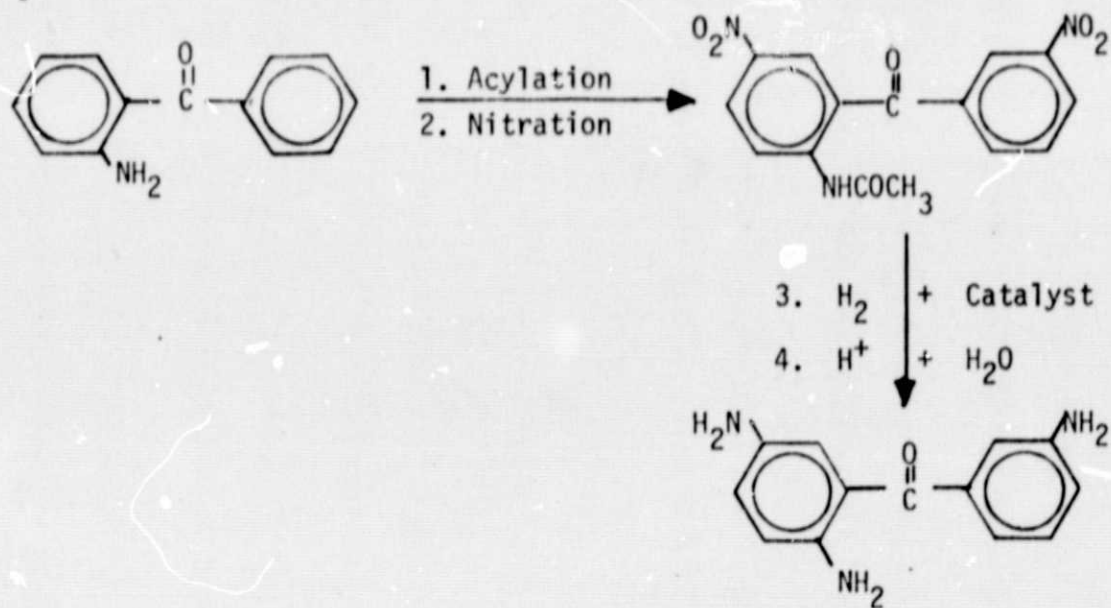
¹ELEMENTAL ANALYSIS OF THE NITROBENZYL- AND AMINOBENZYL BENZENES

Compound ²	Percent Composition			Percent Composition		
	C	H	N	C	H	N
<i>Theoretical</i>	71.28	6.00	6.90	83.68	8.19	8.13
1,2-Bis(<i>m</i> -amino-benzyl)-3,4,5,6-tetramethylbenzene	71.28	5.96		83.39	8.42	
1,2-Bis(<i>p</i> -amino-benzyl)-3,4,5,6-tetramethylbenzene				83.48	8.19	
1,3-Bis(<i>m</i> -amino-benzyl)-2,4,5,6-tetramethylbenzene	70.98	6.08		83.75	8.37	
1,3-Bis(<i>p</i> -amino-benzyl)-2,4,5,6-tetramethylbenzene	71.48	6.15		83.58	8.27	
1,4-Bis(<i>m</i> -amino-benzyl)-2,3,5,6-tetramethylbenzene	71.58	6.29		83.38	8.32	
1,4-Bis(<i>p</i> -amino-benzyl)-2,3,5,6-tetramethylbenzene				83.72	8.43	

¹Analyses performed by Galbraith Laboratories, Inc., Knoxville, Tennessee

²The diamine monomer is the compound named. The analyses are shown in the column labeled "amino analog." The parent nitro compound analysis is shown in the column labeled "nitro analog."

METHOD I



METHOD II

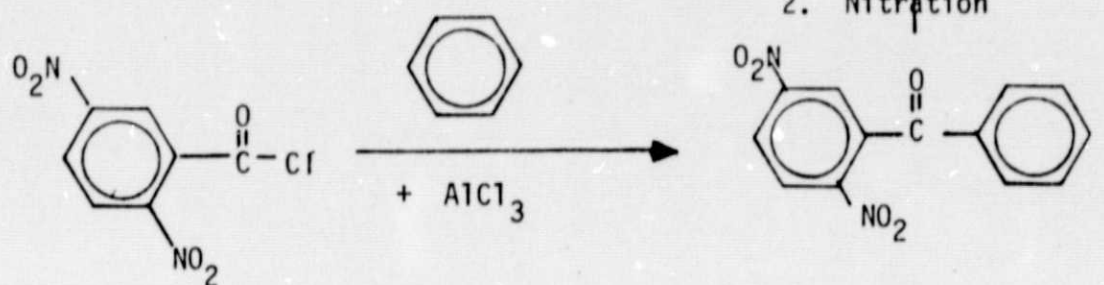


Figure 2. Synthetic Scheme for Preparing 2,5,3'-Triaminobenzophenone.

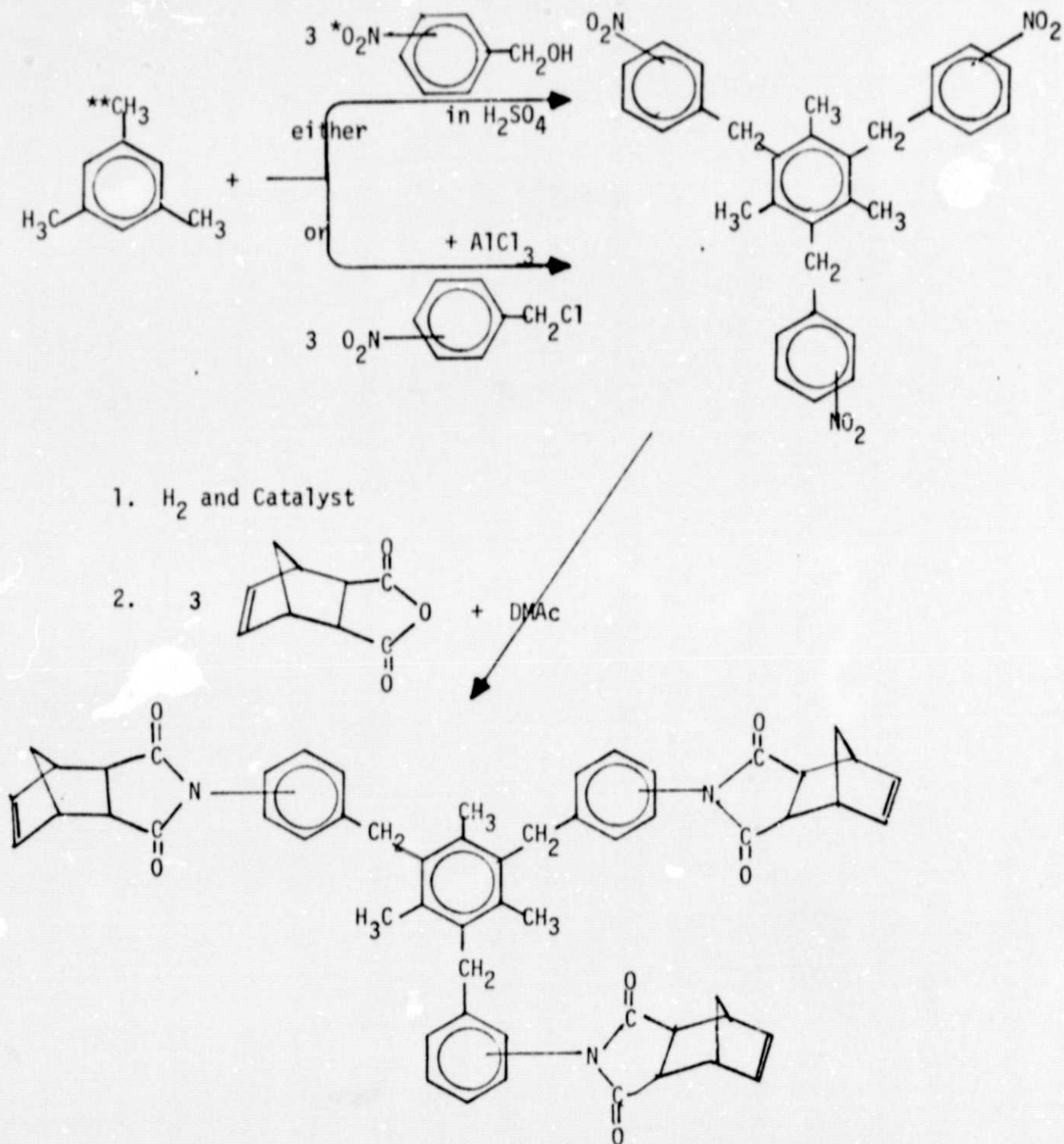
polyimide. Evidence from the TBA analysis suggested that the concept was valid, *i.e.* heating the polyimide to temperatures somewhat greater than its t_g apparently caused cross-linking and destruction of the low initial t_g of the polymer. The cross-linking was thought to have occurred through the acetamido group in the *ortho* position on the diamine monomer portion of the polymer backbone. No further studies were attempted.

C. Imide Monomers for Addition-Type Polyimides

A promising route to polyimide polymers which combine thermal stability with processability has been found in the reaction scheme shown as Figure 3. The trialkyl-substituted benzene starting material can be either trimethyl, triethyl, or triisopropyl benzene and the three alkyl groups can be attached 1,2,3- or 1,2,4- or 1,3,5-. Either a Friedel-Crafts reaction with the nitrobenzyl chloride or a sulfuric acid dehydration with nitrobenzyl alcohol can be used to prepare the trisubstituted trialkyl intermediate. Reduction of the nitro compound leads to a triamine which can then be reacted with anhydrides like 5-norbornene-2,3-dicarboxylic anhydride (nadic anhydride, NAC) to produce a soluble, relatively low-melting monomer. These monomers are attractive for several end-uses.

1. The monomers are powders which potentially could be melt-pressed into desired forms, and continued heating could then be used to effect polymerization through the carbon-carbon double bond in the anhydride rings.

2. The triamines prepared as intermediates in these syntheses could find use as cross-linking or curing agents for epoxide and urethane polymers in adhesives applications.



*The nitro group in the benzyl alcohol or benzyl chloride can be either *ortho*, *meta*, or *para*.

**The trimethyl benzene can be either 1,3,5- or 1,2,3- or 1,2,4-.

Figure 3. Imide Monomers for Addition-Type Polyimides.

3. If some means could be found to cap just one of the amino groups in the triamines with NCA, these substituted diamines would make interesting monomers for the preparation of polyimides. The anhydride thus incorporated into the molecule would provide a means for post-cure cross-linking to increase the glass-transition temperature of the polymer in the final product.

4. If disubstitution of nitroaromatic rings on the tri-alkylbenzene could be achieved, another class of diamine monomers for use in preparing polyimides would be obtained.

All of the possible nitro compounds involving substitution in the *meta*- or *para*- positions on the benzyl rings have been synthesized and subsequently reduced to triamines. The melting points and analyses are given in Tables III and IV for these compounds. Detailed synthetic procedures of example compounds have been described in previous reports (5, 6, 7).

The triamines were further reacted, either with 5-norbornene-2,3-dicarboxylic anhydride or with maleic anhydride, to produce reasonably stable triimide monomers. The results for those compounds which have been prepared and fully characterized are included in Tables III and IV. The procedure for the synthesis of the imide monomers has been described previously (8). The preparation of the imides using maleic anhydride appears to be more temperature-sensitive and therefore more difficult. The imides derived from maleic anhydride are also less stable to heat, apparently undergoing polymerization much more readily. For this reason, it has been difficult to establish reproducible melting points for these compounds.

TABLE I: I

THE MELTING POINTS OF NITROBENZYL- AND AMINOBENZYL BENZENES
AND IMIDE DERIVATIVES WITH NCA AND MA

Compound ¹	Nitro Analog T, °C	Amino Analog T, °C	Imide with NCA ² T, °C	Imide with MA ³ T, °C
1,2,3- <i>Tris</i> (<i>m</i> -amino- benzyl)-4,5,6-tri- methylbenzene	188-190	100-120	178-182	130(?)
1,2,3- <i>Tris</i> (<i>p</i> -amino- benzyl)-4,5,6-tri- methylbenzene	224	185	215	
1,2,4- <i>Tris</i> (<i>m</i> -amino- benzyl)-3,5,6-tri- methylbenzene	188	100-120	175	150-160
1,2,4- <i>Tris</i> (<i>p</i> -amino- benzyl)-3,5,6-tri- methylbenzene	206	192-195	270	
1,3,5- <i>Tris</i> (<i>m</i> -amino- benzyl)-2,4,6-tri- methylbenzene	179-181	182-183	167-170	260-270
1,3,5- <i>Tris</i> (<i>p</i> -amino- benzyl)-2,4,6-tri- methylbenzene	226	230	178-180	

¹The diamine monomer is the compound named. The melting points for these compounds are shown in the column labeled "amino analog." The parent nitro compound's melting point is given in the column labeled "nitro analog."

²The imide product of the amino analog with 5-norbornene-2,3-dicarboxylic anhydride.

³The imide product of the amino analog with maleic anhydride.

TABLE IV

THE ELEMENTAL ANALYSIS OF THE NITROBENZYL-,
AMINO BENZYL-, AND IMIDO BENZYL BENZENES

Compound ¹	Percent Composition			Percent Composition			Percent Composition		
	C	H	N	C	H	N	C	H	N
Theoretical	Nitro Analog			Amino Analog			Imido Analog ²		
	68.56	5.18		82.72	7.64	9.65	78.33	5.88	4.80
1,2,3-Tris(m-aminobenzyl)-4,5,6-trimethylbenzene	68.72	5.31		82.90	7.78	9.32	78.22	5.95	5.02
1,2,3-Tris(p-aminobenzyl)-4,5,6-trimethylbenzene				82.66	7.87				
1,2,4-Tris(m-aminobenzyl)-3,5,6-trimethylbenzene	68.83	5.40		82.68	7.64	9.19	78.89	5.92	5.12
1,2,4-Tris(p-aminobenzyl)-3,5,6-trimethylbenzene				82.41	7.76				
1,3,5-Tris(m-aminobenzyl)-2,4,6-trimethylbenzene	68.26	5.34		82.84	7.50		78.44	5.96	4.80
1,3,5-Tris(p-aminobenzyl)-2,4,6-trimethylbenzene	67.80	5.34		82.38	7.55	9.64			

¹The diamine monomer is the compound named. The analyses for these compounds are shown in the column labeled "amino analog." The parent nitro compound's analysis is shown in the column labeled "nitro analog." The analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

²This is the imide product of the amino analog with 5-norbornene-2,3-dicarboxylic anhydride.

An evaluation of the imide monomers in addition-type polymers is just being undertaken. Shown as Figure 4 is a differential scanning calorimeter (DSC) run made on the nadic anhydride triimide derivative of 2,4,6-*tris*(*m*-aminobenzyl)-1,3,5-trimethyl benzene. The curve indicates that melting took place in the expected temperature range and that other changes, taken to be addition polymerization, occurred around 315 °C. Reheating the sample showed the absence of a melting point, confirming that polymerization had taken place. A hard, resinous product was obtained which has yet to be characterized.

The complete characterization of these materials is planned, with the hope that a publication can be obtained, even though grant support for this project has been discontinued.

III. Summary

A. A series of diamines with two aromatic rings were synthesized and used to prepare polyimides. High thermal stability was retained but a marked lowering of the glass-transition temperature was achieved through asymmetry in the diamine monomers. An extensive publication which included these results appeared in 1976 (1). A portion of this work was undertaken by the Principal Investigator as a NASA-ASEE Summer Faculty Research Fellow at NASA-LaRC during the summers of 1972 and 1973. Dr. Helen M. Gager also carried out portions of the work while employed as a part-time post-doctoral research associate with the Principal Investigator, using funds provided by this grant. Dr. Gager is now chairman of the Chemistry Department at Sweet Briar College in Sweet Briar, Virginia.

RUN NO. DATE

OPERATOR

SAMPLE:

ATM (at)

FLOW RATE

T-AXIS

SCALE, °C/in 50

PROG. RATE, °C/min

HEAT COOL ISO

SHIFT, in 0

DTA-DSC

SCALE, °C/in

(mcal/sec)/in

WEIGHT, mg

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PolymerizationMelting
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Figure 4. A Differential Scanning Calorimeter Analysis of the Triimide Formed From 5-Norbornene-2,3-Dicarboxylic Anhydride and 1,3,5-Tris(*n*-aminobenzyl)-2,4,6-trimethylbenzene.

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3. Diamines containing three aromatic rings and additional elements of asymmetry failed to produce polyimides with glass-transition temperatures lower than those reported for the two-ring diamines. This work was carried out by Mr. David Joslyn as a thesis for the M.S. degree in Chemistry at Virginia Commonwealth University. He is currently writing his thesis. Mr. Joslyn was supported for about fourteen months as a Graduate Student Research Assistant with funds from this grant.

C. Diamines containing extra functionality to permit post-cure cross-linking when incorporated into polyimides were studied. Most of the work in this area was performed by Dr. Junaaid Siddiqui, who was employed as a post-doctoral research associate of the Principal Investigator with funds from this grant. Dr. Siddiqui is now engaged in polymer research and development as a chemist with ICI Americas in Hopewell, Virginia.

D. An interesting series of triimide monomers suitable for the preparation of addition-type polyimides has been synthesized. This work, together with the three ring diamines described above, led to a NASA Tech Brief (9) as well as a Patent Application (8). The initial experiments were carried out by an undergraduate research assistant, Mr. Ralph Schaffer, who was employed using funds from this grant. Mr. Schaffer went on to dental school at the University of Pittsburgh. The bulk of this work, however, has been accomplished by an M.S. Chemist, Ms. Li Ching Shih, who was employed over about a two year period as a research associate, and her support came from grant funds. Ms. Shih is currently pursuing the Ph.D. degree in Chemistry at Virginia Commonwealth University.

E. A host of undergraduate chemistry majors have worked on phases of the project during the past six years, and they are too numerous to mention. Most of them were taking Chemistry 497, "Independent Study," and did not receive pay for their work. A few were employed by the hour as research assistants or technicians with funds from the grant.

F. Grant support terminated on March 31, 1978. However, four undergraduate chemistry majors are continuing the investigation for academic credit in Chemistry 497. It is the goal of the Principal Investigator to see all the projects terminated successfully in the form of publications.

